Long-Lifetime Aqueous Soluble Organic Flow Battery Development

Research supported by US DOE award DE-AC05-76RL01830 through PNNL subcontract 535264 - $225k/yr.

PI: Michael J. Aziz, Harvard School of Engineering and Applied Sciences

- Context from prior research: Importance of cost and lifetime; measuring long lifetimes
- Measuring capacity fade <1%/yr: DPivOHAQ
- Determining the predominant decomposition mechanism of anthraquinones
- Lifetime extension strategies and results
- Cost-lifetime tradeoff: DCDHAQ

Primary Requirements for Aqueous-Soluble Organics

Requirements

CATEGORY	SPEC	PROSPECTS
Cell voltage	>~ 1.0 V	Several anthraquinones
Aqueous solubility	>~ 1 M e^- (27 Ah/L)	Several anthraquinones
Redox kinetics	Kinetic ASR << membrane ASR	Most anthraquinones
Chemical stability	Fade rate <~ 10%/yr	Very few AQs
Cost	Mass production cost <~$50/kAh	Very few AQs

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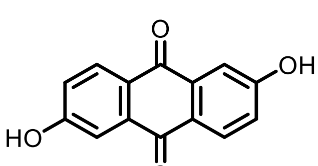
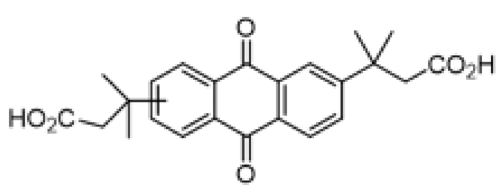
Candidates

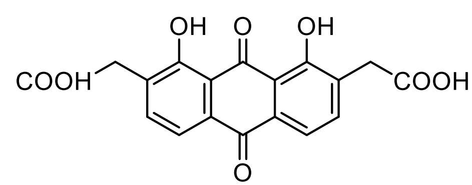
Negolyte Species	**Mass Production Cost ($/kAh)**	**Fade Rate** Initial → With lifetime extension
DPivOHAQ	~100	0.0018%/day (0.66%/yr)
DHAQ	~ 26	5.6%/day → 0.8%/day → 0.05%/day (18%/yr)
DCDHAQ	40-50	0.03%/day (11%/yr) →? →?
Posolyte Species	**Mass Production Cost ($/kAh)**	**Fade Rate**
$Fe(CN)_6^{3-/4-}$	21-26	--



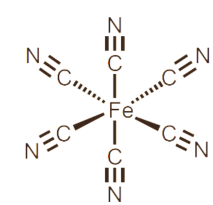
DHAQ



DPivOHAQ



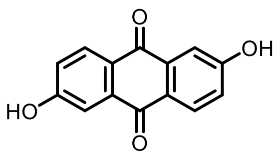
DCDHAQ

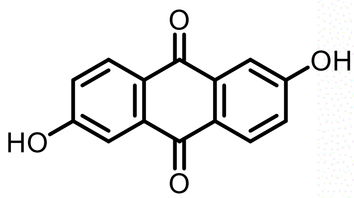


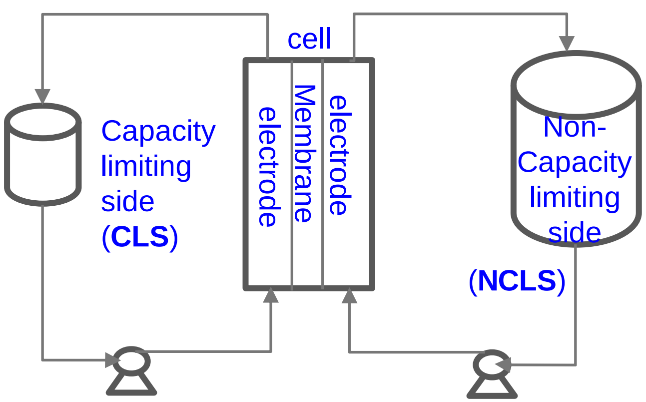
$Fe(CN)_6$

Context from our Prior Research: Capacity Fade Rate Depends Mainly on SOC, *not* Cycle Rate

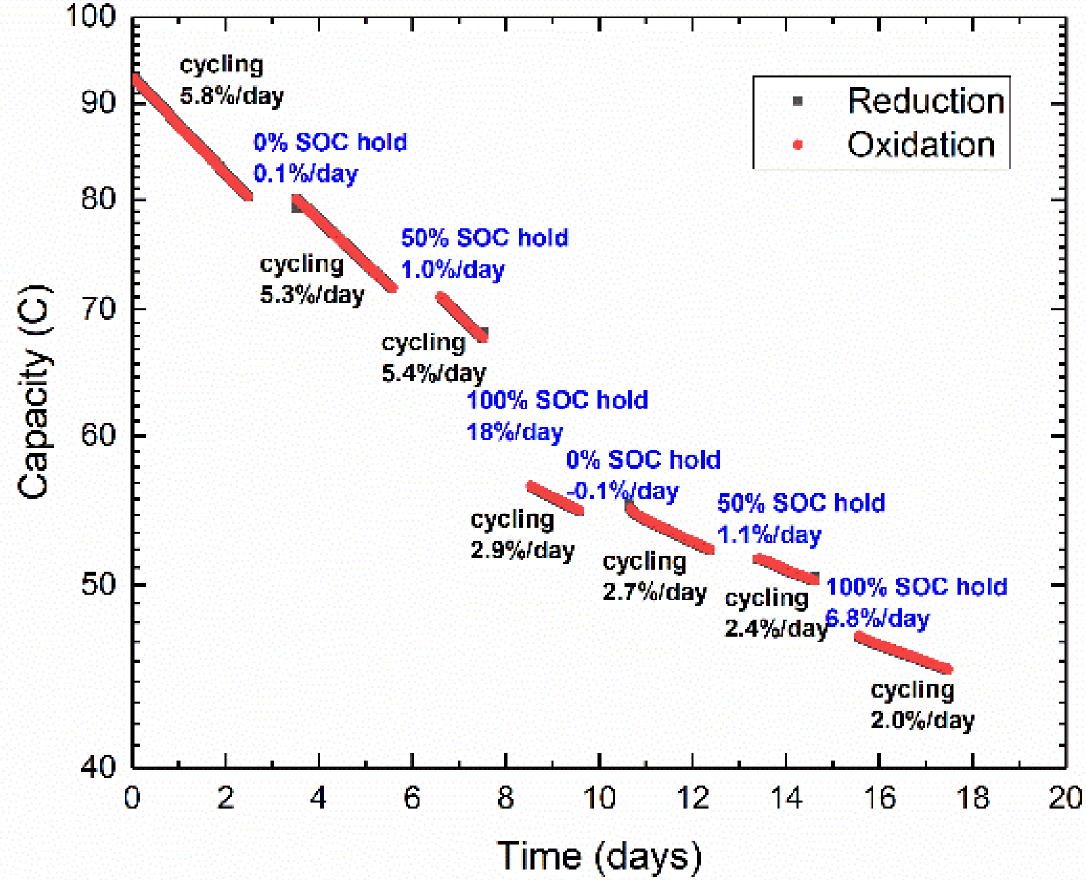
Unbalanced compositionally-symmetric cell cycling experiment
Both sides 2,6-DHAQ, 50% SOC,
0.1 M in 1 M KOH, glove box (**OCV = 0**)







2,6-DHAQ vs. 2,6-DHAQ



Marc-Antoni Goulet & M.J. Aziz, "Flow Battery Molecular Reactant Stability Determined by Symmetric Cell Cycling Methods", *JES* **165**, A1466 (2018)

Context from our Prior Research: Potentiostatic Cycling Eliminates Capacity Fade Artifact from ASR Drift

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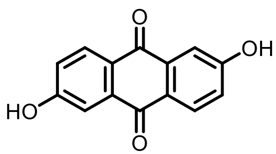
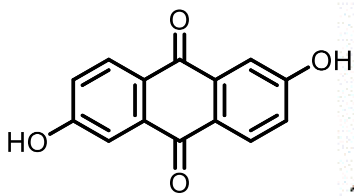
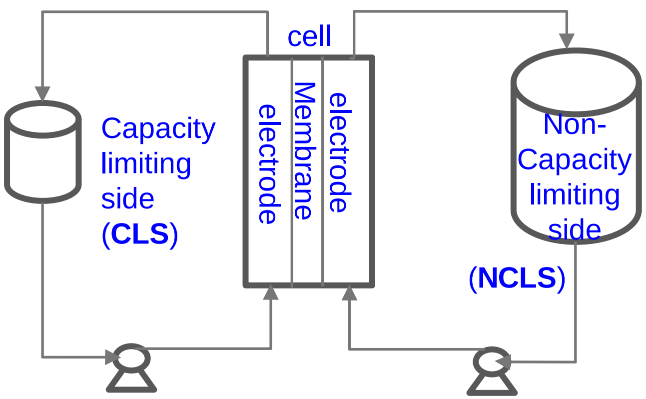
Both sides 2,6-DHAQ, 50% SOC,
0.1 M in 1 M KOH, glove box (**OCV = 0**)

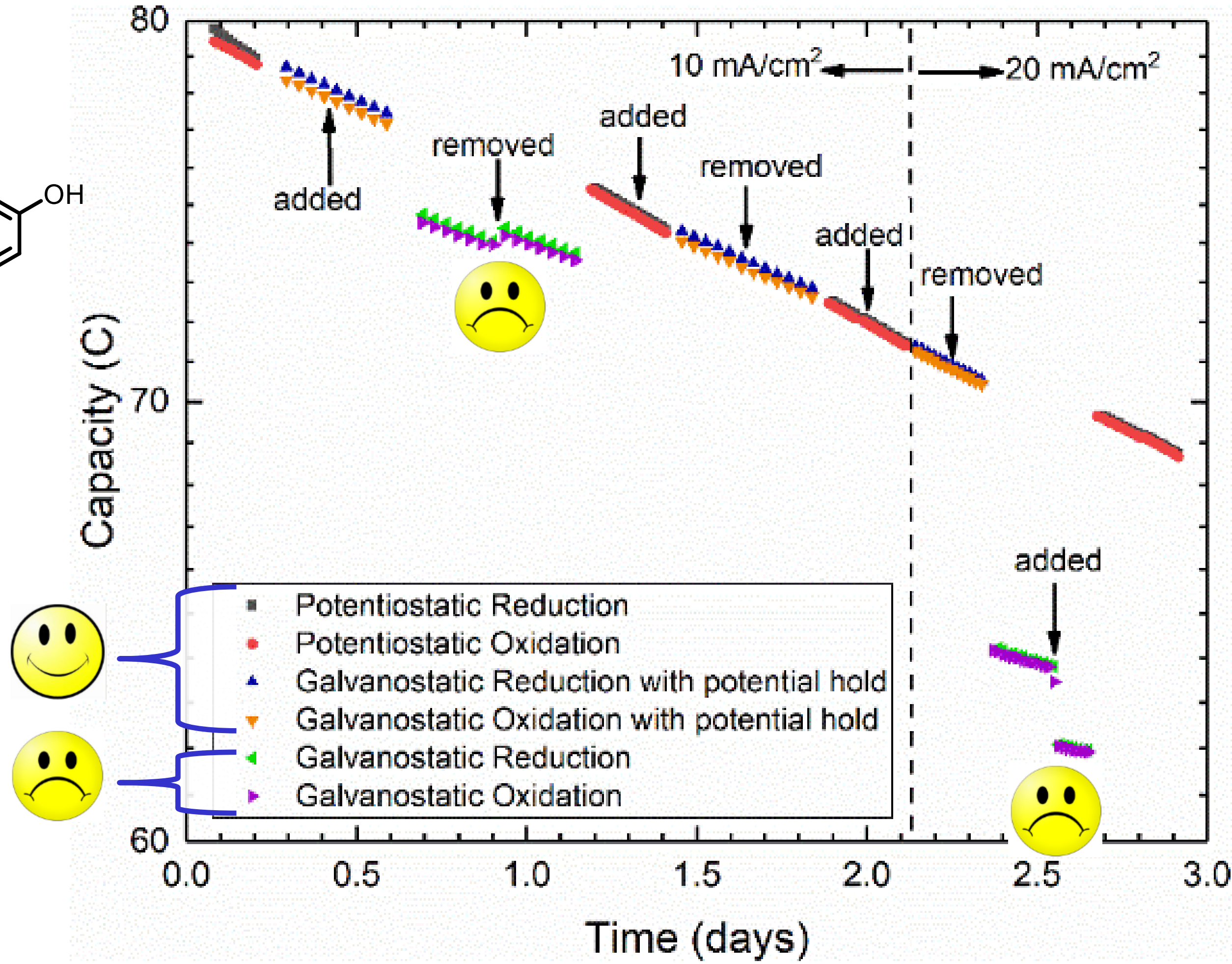






Marc-Antoni Goulet & M.J. Aziz, “Flow Battery Molecular Reactant Stability Determined by Symmetric Cell Cycling Methods”, *JES* **165**, A1466 (2018)

0.13 Ω added/removed in series*



*represents 25% increase in membrane ASR

Harvard Milestones, 9/10/2020—9/9/2021

Task 1. Advanced characterization.

In the area of flow cell performance characterization, Harvard shall support continued development and refinement of methods to reliably and reproducibly measure very slow fade rates in ASO RFBs. The tasks include precise characterization of molecular decomposition and crossover.

Year 1 Milestone:
(1.1) Develop methods to reliably measure capacity fade rates as low as 2%/year

- Demonstrated capacity fade rate of 0.66%/yr (0.0018%/day)

Task 2. Electrolyte development.

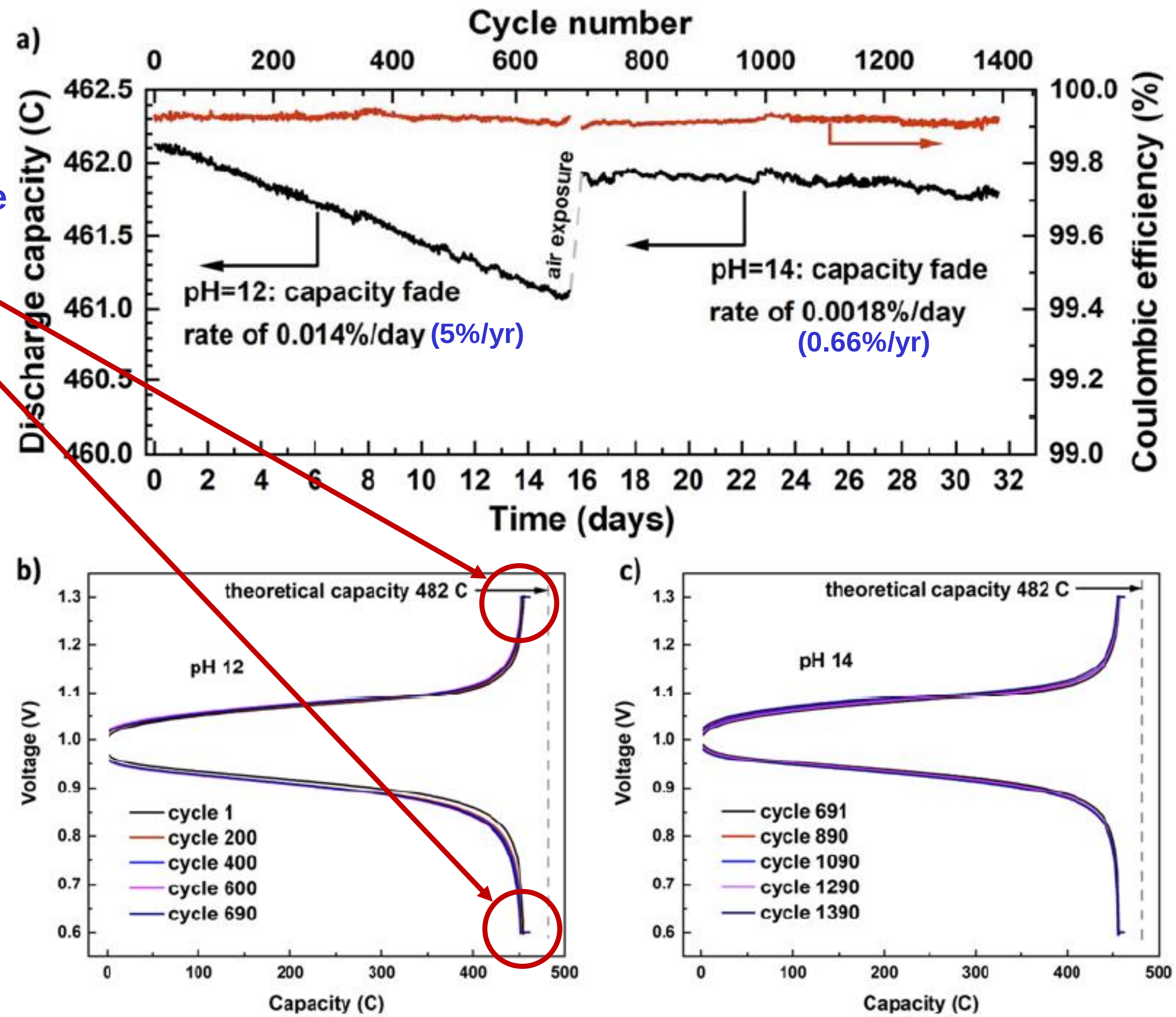
In the area of electrolyte development, Harvard shall support continuous efforts to innovate on redox-active molecules, counter-ions, supporting electrolytes, and membranes in order to improve the performance of ASO RFBs. The tasks include understanding molecular decomposition mechanisms and developing methods to extend ASO lifetime, examining different functionalization and their effect on capacity fade rate through molecular lifetime, studying the permeability of reactants through membranes and its effect on the capacity retention rate through crossover, and exploring mixtures of counter-ions in order to raise ASO solubility.

Year 1 Milestone:
(1.2) Demonstrate three methods of extending ASO lifetime

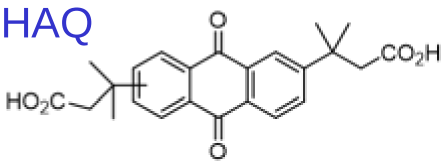
- Restrict max SOC
- Expose to air
- Raise pH
- Expose to oxidized posolyte
- Oxidize electrochemically

Reliable Measurements of Extremely Low Fade Rates

Galvanostatic (100 mA/cm^2) cycling;
Potential hold at end of each half-cycle
until current < 2 mA/cm^2

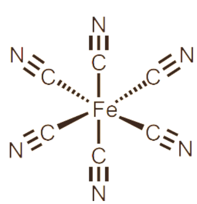


Negative Species:
DPivOHAQ



DPivOHAQ

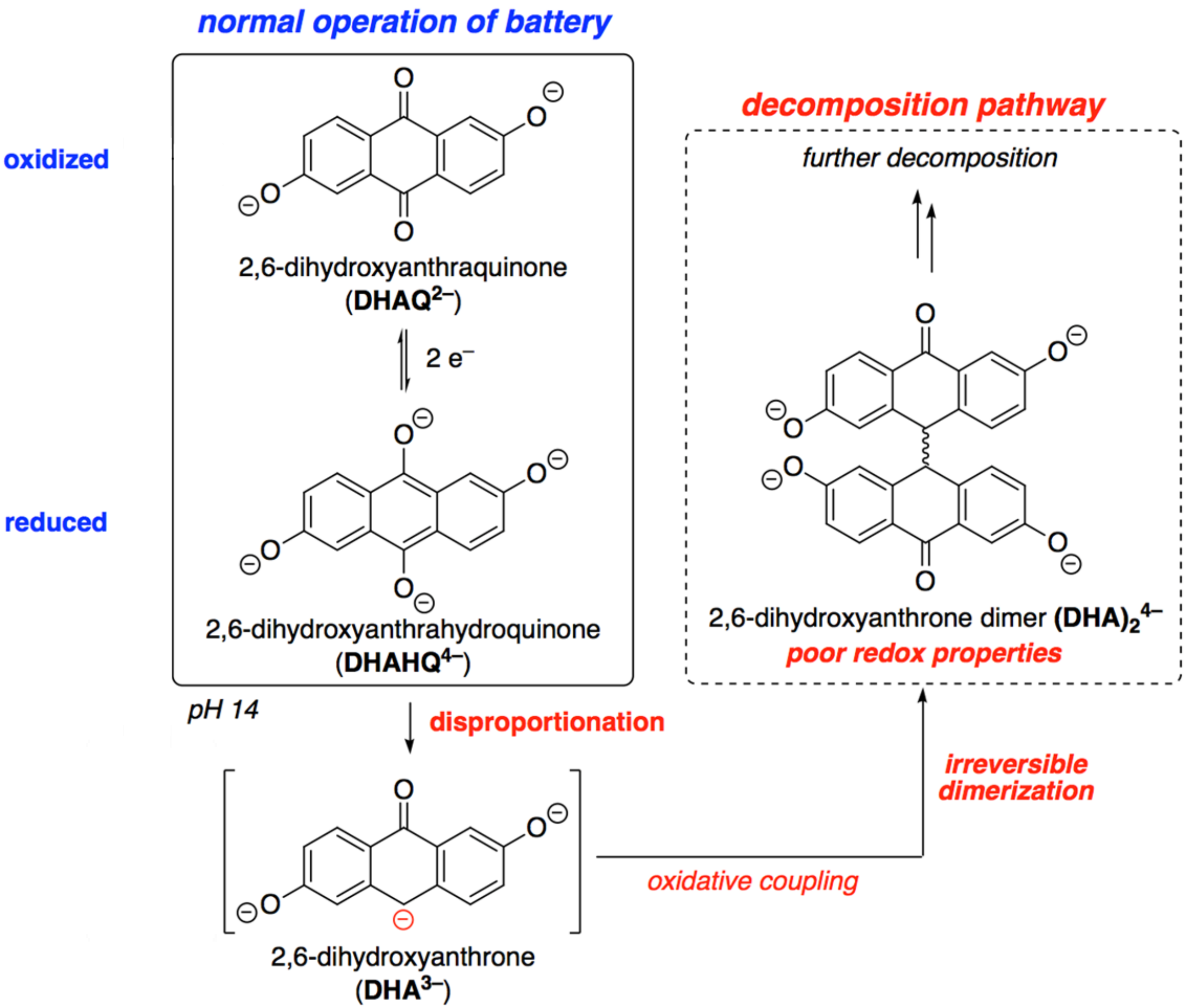
Positive Species:
$Fe(CN)_6$



Min Wu, Yan Jing, A.A. Wong, E.M. Fell, S. Jin, Z. Tang, R.G. Gordon and M.J. Aziz, "Extremely Stable Anthraquinone Negolytes Synthesized from Common Precursors" **Chem** *6*, 1432 (2020)

Predominant Anthraquinone Decomposition Mechanism

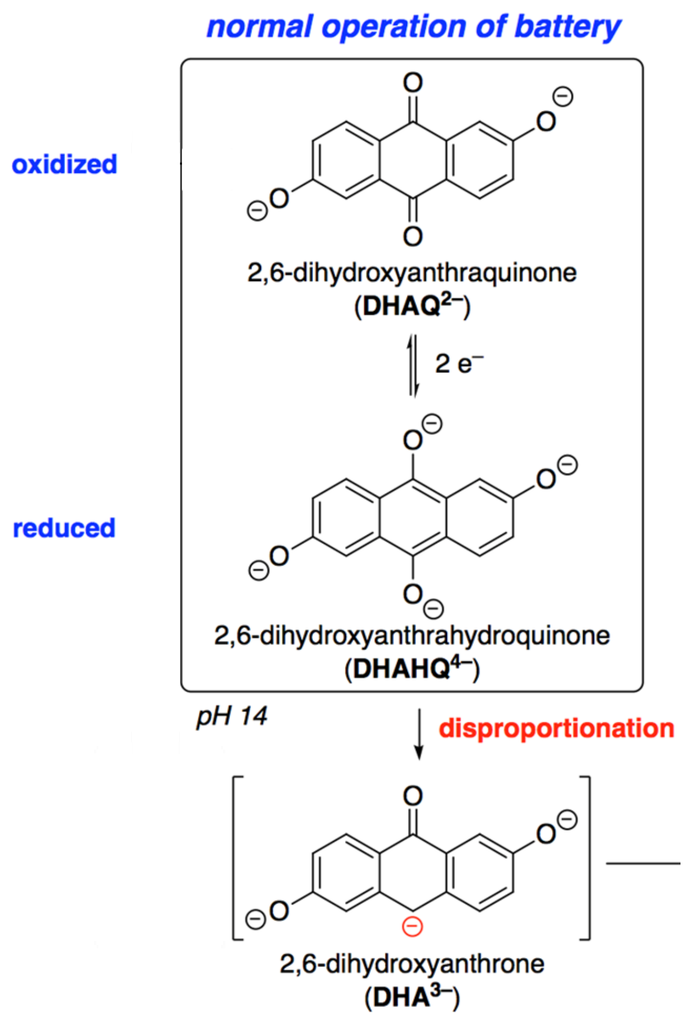
Prototype: DHAQ at pH >~12



Marc-Antoni Goulet, Liuchuan Tong, *et al.*, "Extending the Lifetime of Organic Flow Batteries via Redox State Management", *J. Am. Chem. Soc.* **141**, (2019); https://doi.org/10.1021/jacs.8b13295

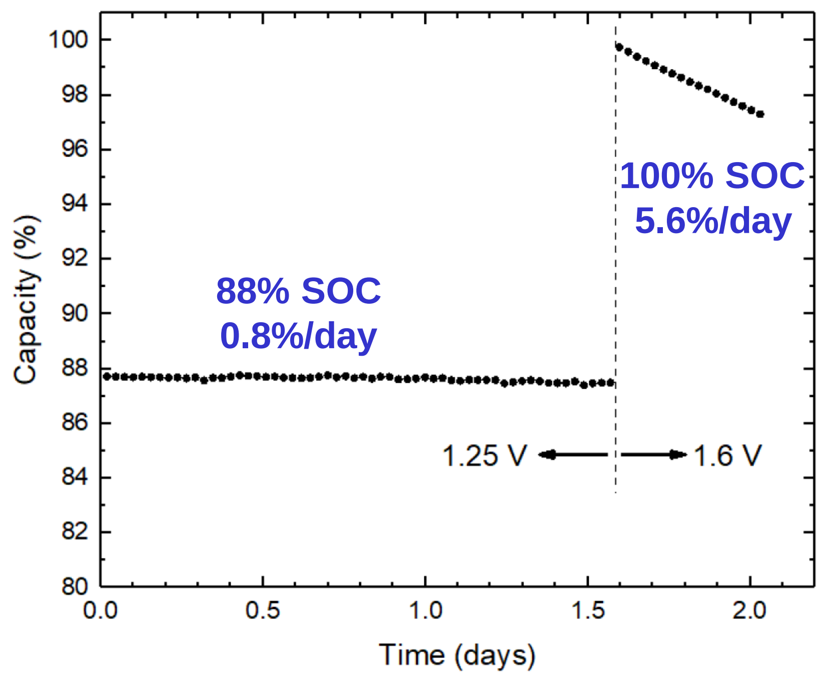
Decomposition Suppression. Strategy #1: Restricted SOC Range

Prototype: DHAQ at pH >~12



Strategy #1: Restrict SOC range.
Accessing only ~88% of theoretical capacity cuts anthrone formation rate.

→Cuts fade rate by 7×



5.6%/day → 0.8%/day

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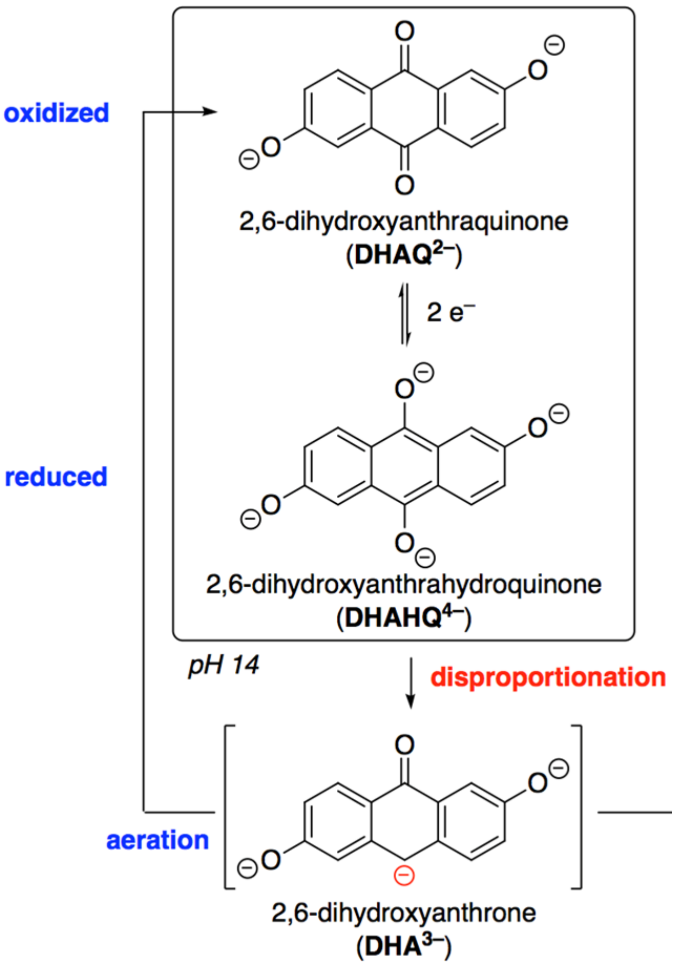
Strategy #2: Regeneration by Air Exposure

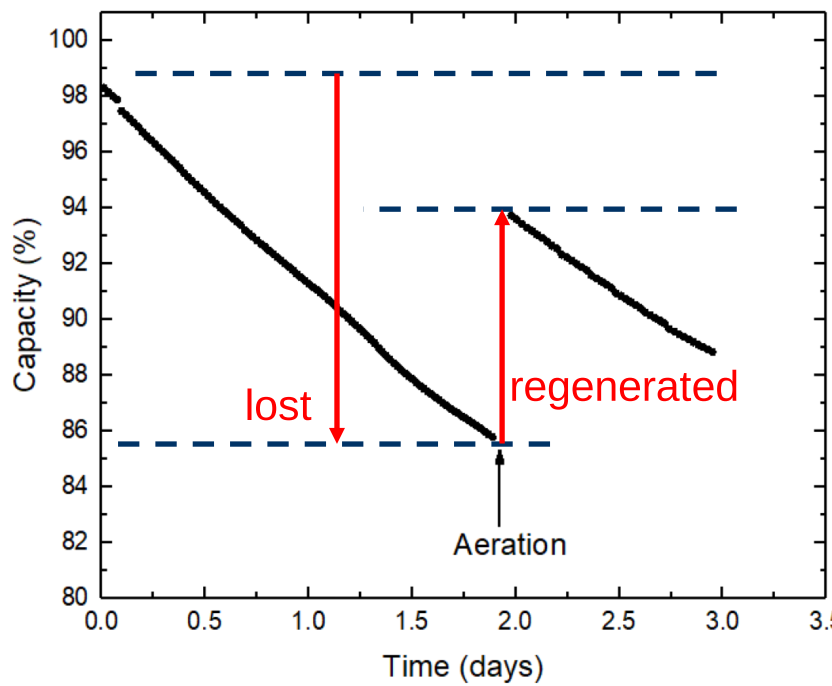
Prototype: DHAQ at pH >~12

normal operation of battery



Strategy #2: Aerate as anthrone forms to chemically oxidize back to DHAQ

→Regenerates 70% of lost capacity



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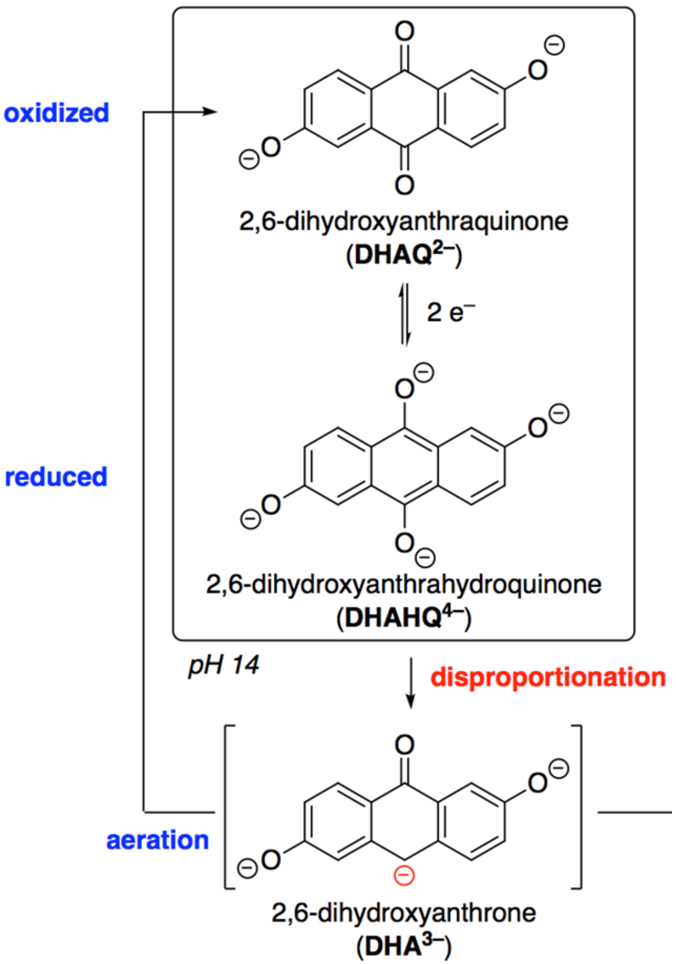
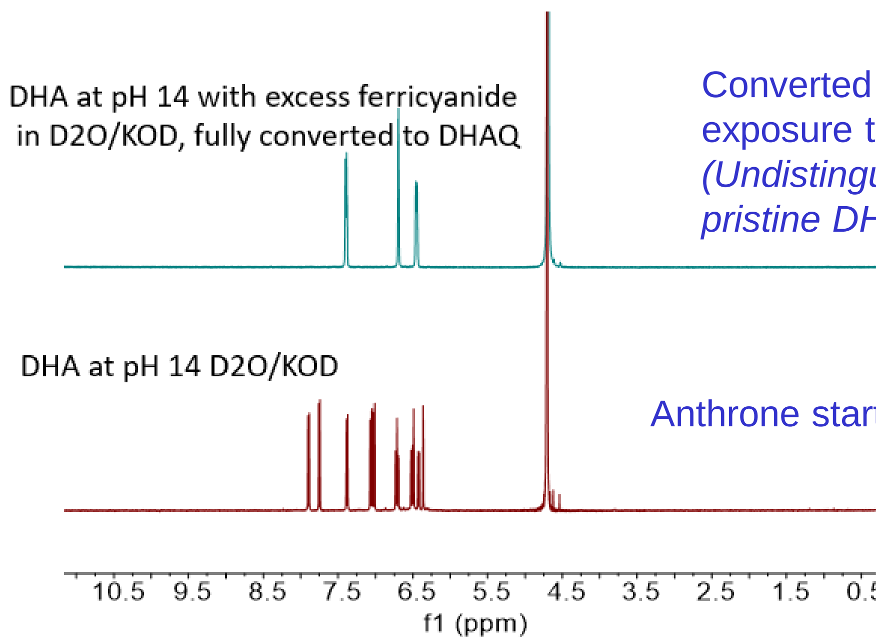
Strategy #3: Oxidation by Oxidized Posolyte

Prototype: DHAQ at pH >~12

normal operation of battery



Strategy #3: Expose to ferricyanide to chemically oxidize back to DHAQ



Converted to DHAQ by exposure to ferricyanide *(Undistinguishable from pristine DHAQ)*

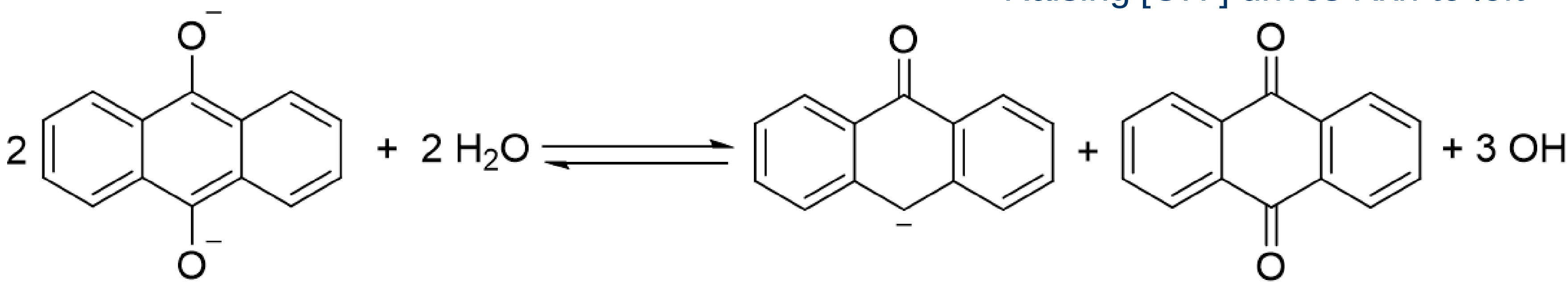
Anthrone starting material

^{1}H NMR spectra

Strategy #4: Raise pH

Prototype: DHAQ at pH >~12

Le Chatelier's Principle:
Raising $[OH^-]$ drives Rxn to left



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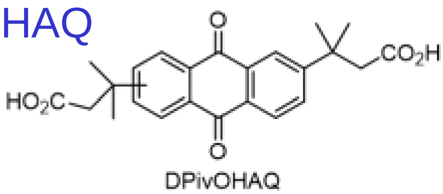
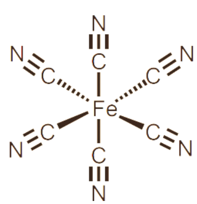
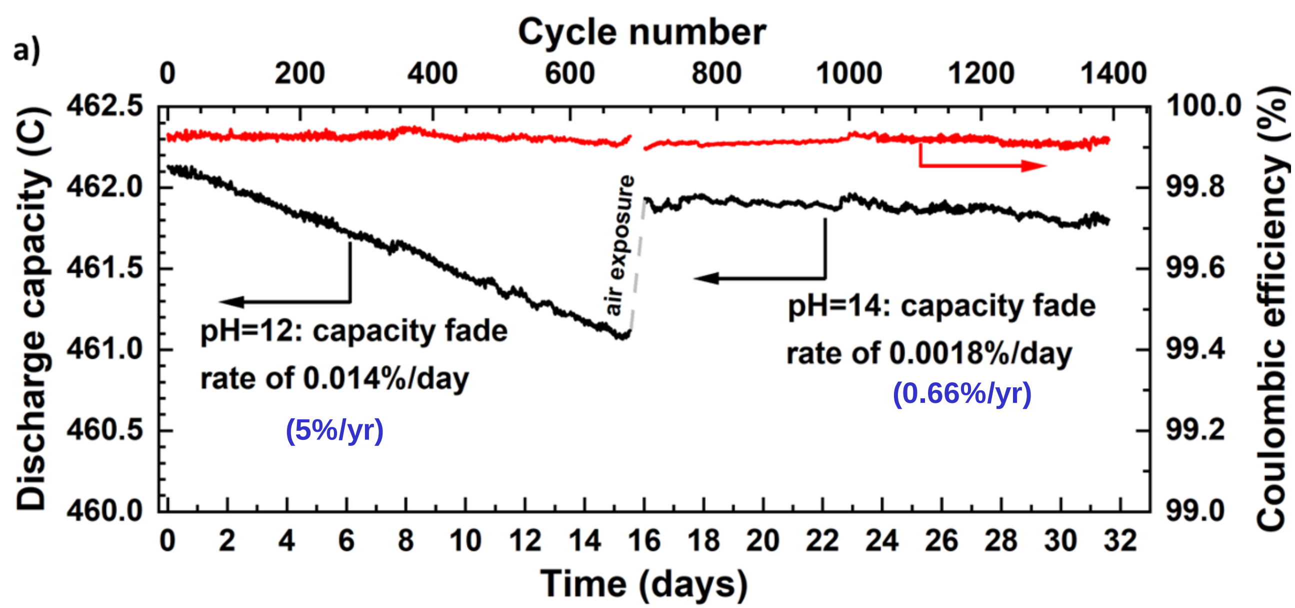


Positive Species: $Fe(CN)_6$





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Strategy #5: Electrochemical Oxidation

Deep discharge / reverse polarization to electrochemically oxidize negolyte

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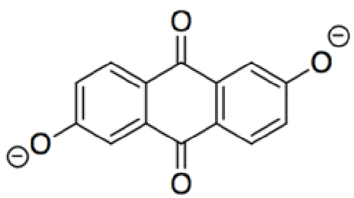

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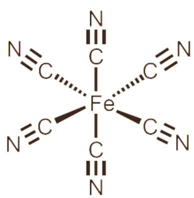
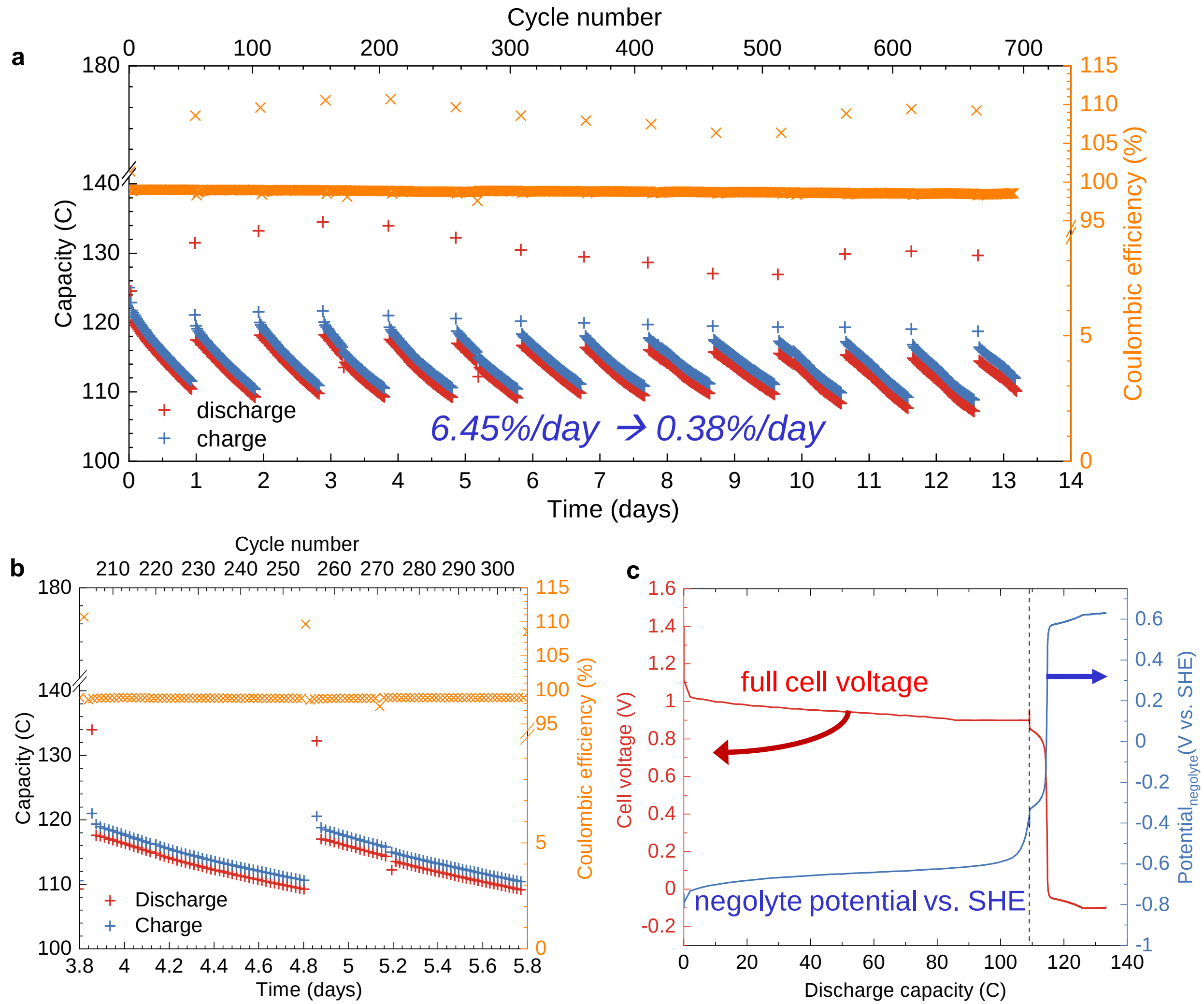




➔ Electrochemical oxidation cuts fade rate by 20x

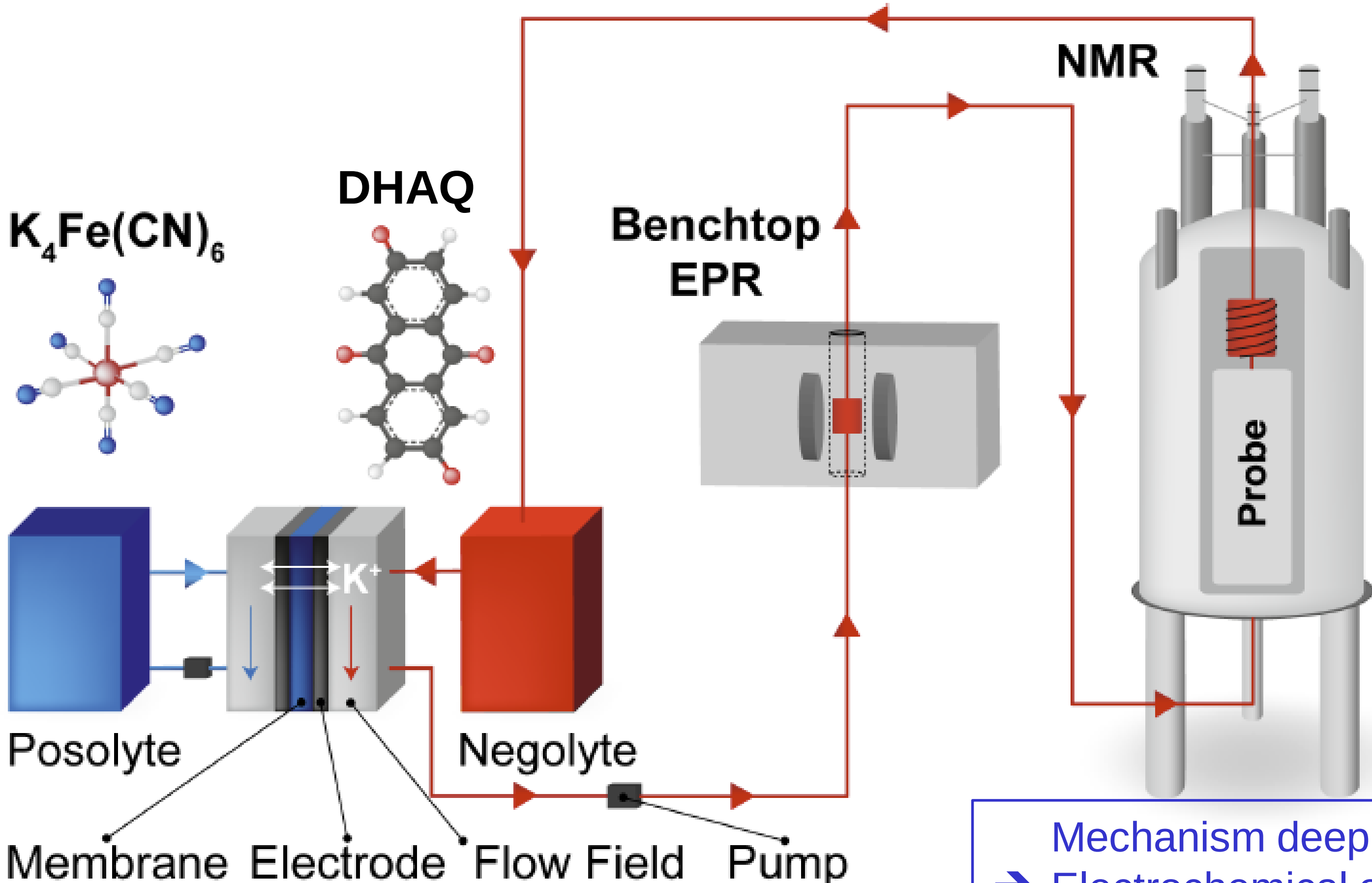
Thanks to mechanism deep dive

Yan Jing, Evan Wenbo Zhao, *et al.*, **Clare P. Grey**, R.G. Gordon, M.J. Aziz, "Electrochemical Regeneration of Anthraquinones for Lifetime Extension in Flow Batteries", *submitted;* https://doi.org/10.33774/chemrxiv-2021-x05x1

Enabling a Mechanism Deep Dive

In-situ, real-time monitoring of DHAQ-related molecular conversions

→ *Collaboration with Clare Grey, Cambridge University*



Mechanism deep dive
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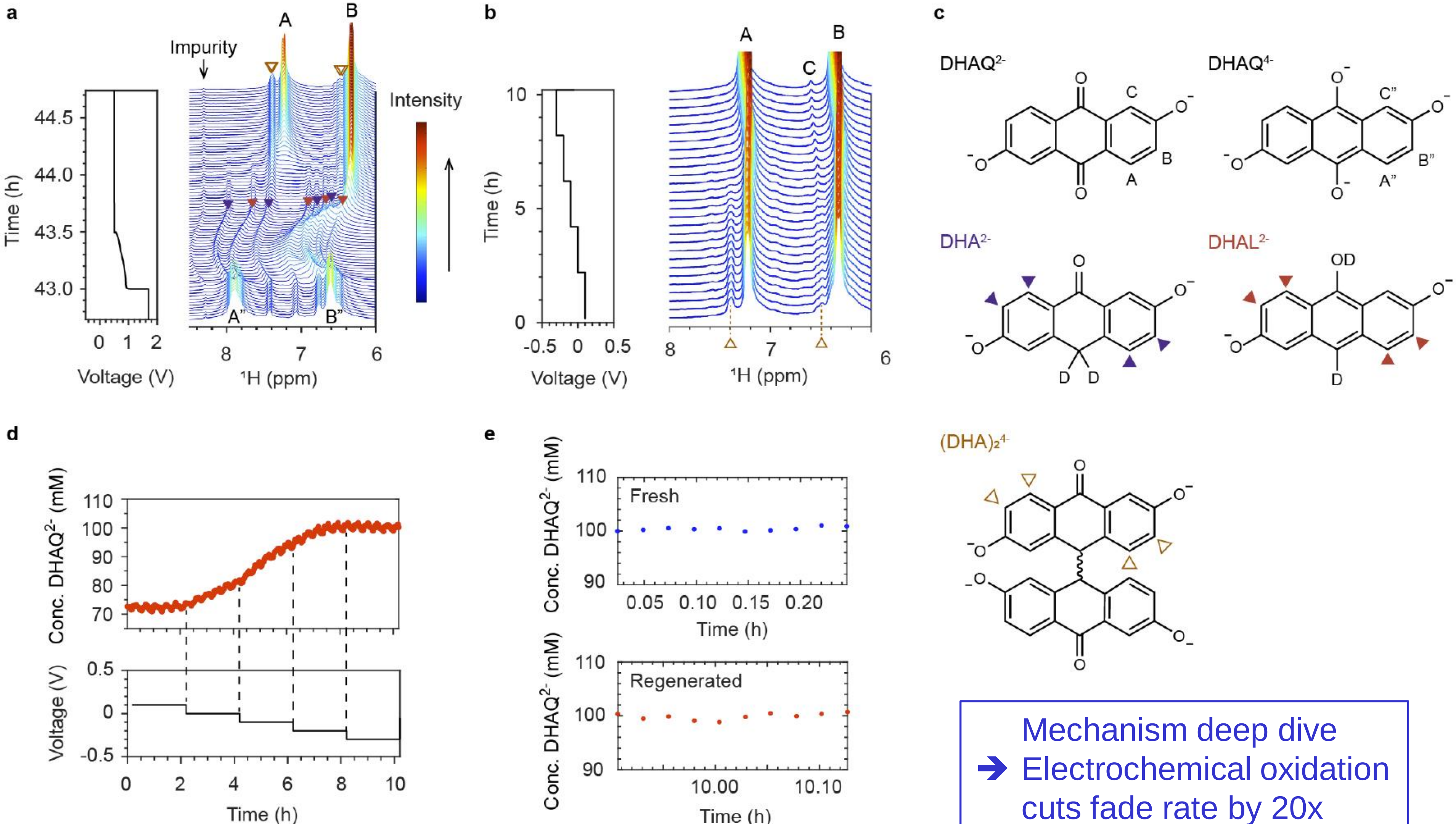

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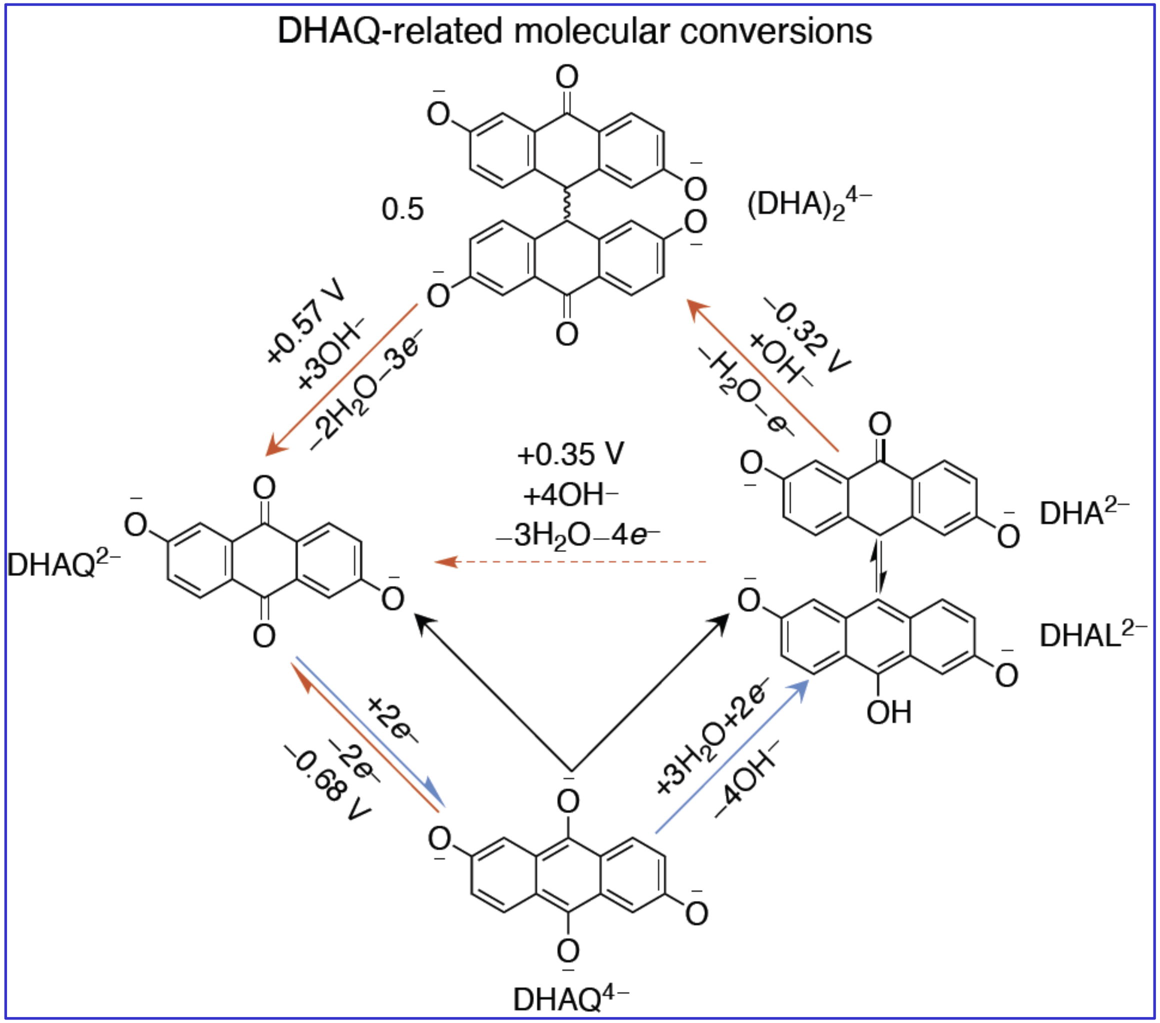

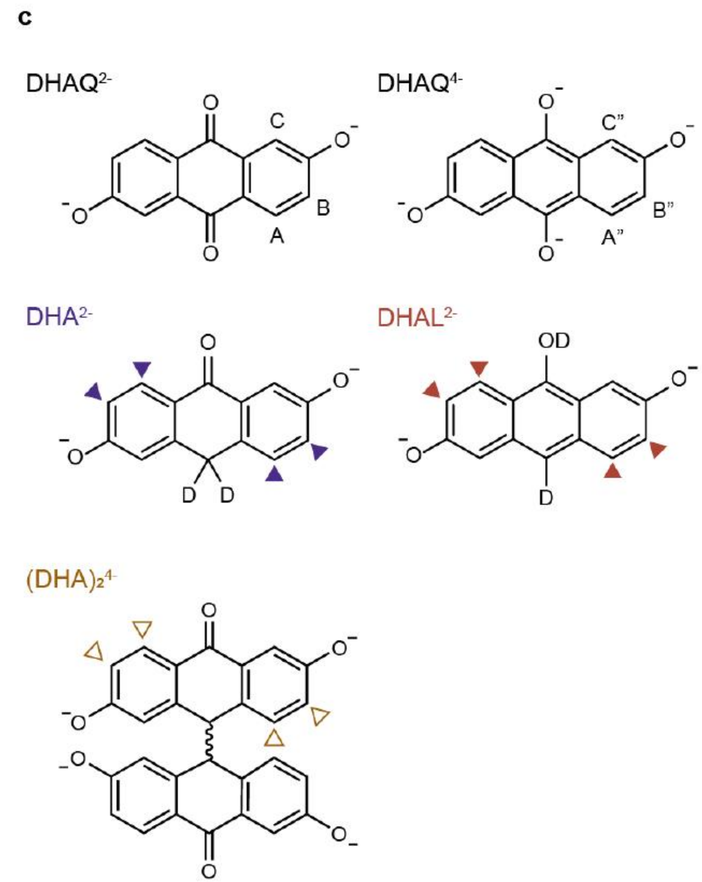

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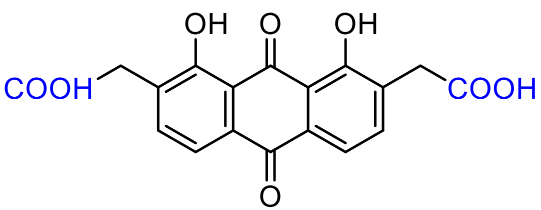
Trading off Lifetime vs. Mass Production Cost: DCDHAQ

Negative Species:
DCDHAQ (~$40-50/kAh)



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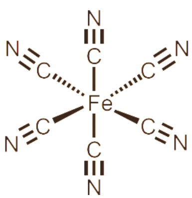

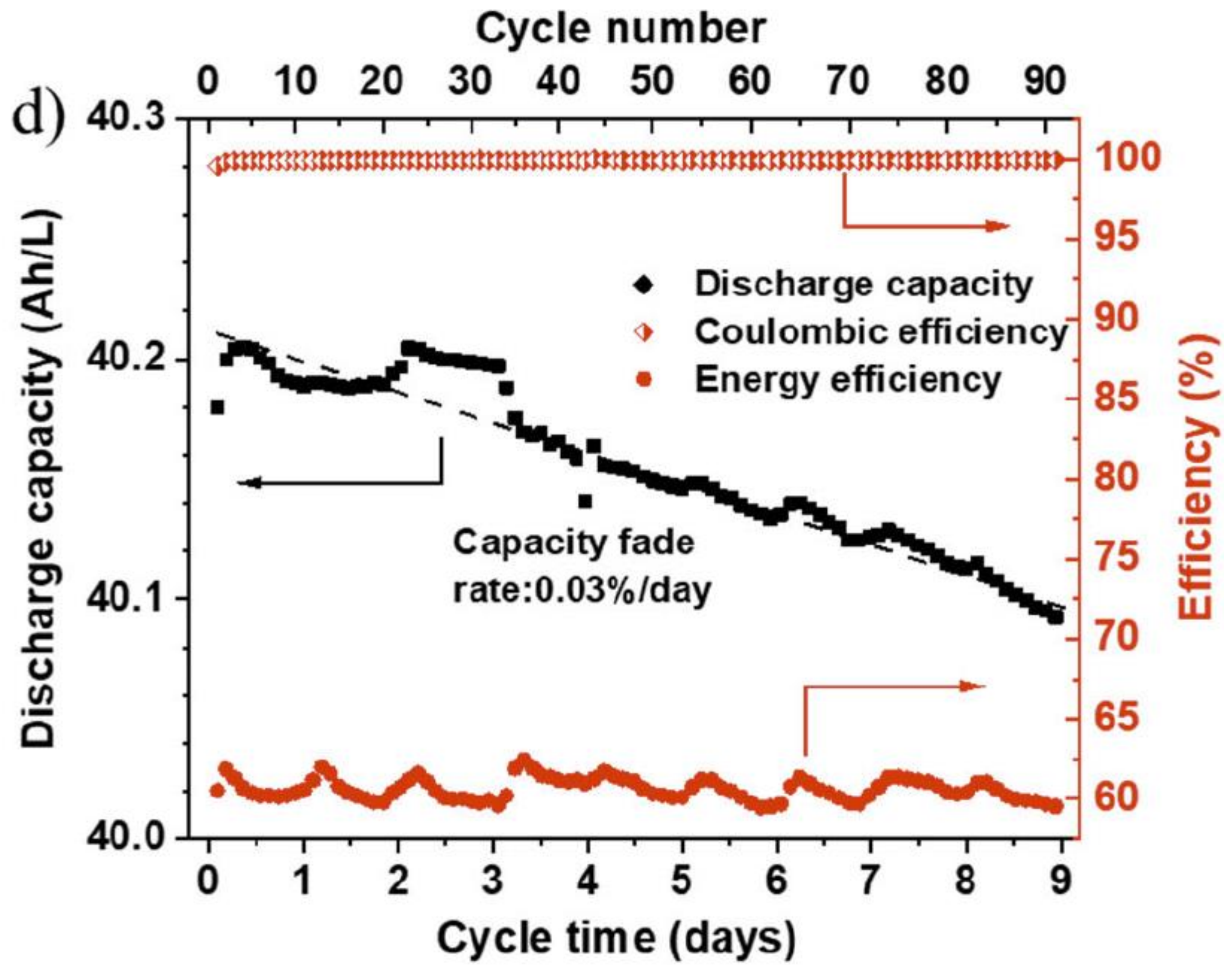

TBD: Effectiveness of lifetime extension strategies

QUINO ENERGY *Harvard spinout*

M. Wu, M. Bahari, E.M. Fell, R.G. Gordon and M.J. Aziz, "High-performance anthraquinone with potentially low cost for aqueous redox flow batteries", *submitted*

Publications acknowledging OE Support

*M. Wu, Y. Jing, A.A. Wong, E.M. Fell, S. Jin, Z. Tang, R.G. Gordon and M.J. Aziz, "Extremely Stable Anthraquinone Negolytes Synthesized from Common Precursors" *Chem* **6**, 1432 (2020); https://doi.org/10.1016/j.chempr.2020.03.021

*Y. Jing, M. Wu, A.A. Wong, E.M. Fell, S. Jin, D.A. Pollack, E.F. Kerr, R.G. Gordon and M.J. Aziz, "In situ Electrosynthesis of Anthraquinone Electrolytes in Aqueous Flow Batteries", *Green Chemistry* **22**, 6084 (2020); https://doi.org/10.1039/D0GC02236E

M. Wu, M. Bahari, E.M. Fell, R.G. Gordon and M.J. Aziz, "High-performance anthraquinone with potentially low cost for aqueous redox flow batteries" *submitted*

Y. Jing, E.M. Fell, M. Wu, S. Jin, Y. Ji, D.A. Pollack, Z. Tang, D. Ding, M. Bahari, M.-A. Goulet, T. Tsukamoto, R.G. Gordon and M.J. Aziz, "Long-lifetime, potentially low-cost anthraquinone flow battery chemistry developed from study of effects of water-solubilizing group and connection to core" *submitted*; Manuscript posted on ChemRxiv at https://doi.org/10.33774/chemrxiv-2021-0cb4d

Y. Jing, E.W. Zhao, M.-A. Goulet, M. Bahari, E. Fell, S. Jin, A. Davoodi, M. Wu, C.P. Grey, R.G. Gordon and M.J. Aziz, "Electrochemical regeneration of anthraquinones for lifetime extension in flow batteries" *submitted;* Manuscript posted on ChemRxiv at https://doi.org/10.33774/chemrxiv-2021-x05x1